

CLAIMS

5 1. A catalyst for addition polymerisation of olefinically unsaturated monomers comprising:

10 a) A first compound

MY

where: M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand.

Y is a monovalent divalent or polyvalent counterion;

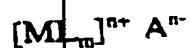
15 b) An initiator compound comprising a homolytically cleavable bond with a halogen atom; and

c) An organodiimine, where at least one of the nitrogens of the diimine is not part of an aromatic ring.

20 2. A catalyst for addition polymerisation of olefinically unsaturated

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- 10



**where:**

$M \neq$  a transition metal of low valency state

L = an organodiimine where at least one of the nitrogens of the diimine is not a part of an aromatic ring.

**A** = an anion

**n = an integer of 1 to 3**

$m =$  an integer of 1 to 2, and

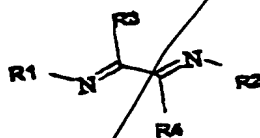
- 15

2.  
3.

A catalyst according to ~~any previous claim~~ wherein the

organodiimine is selected from:

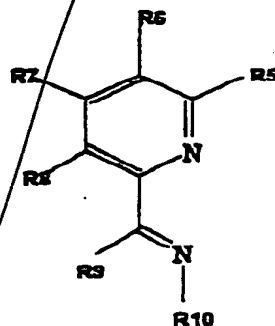
a 1,4-diaza-1,3-butadiene



Formula 24

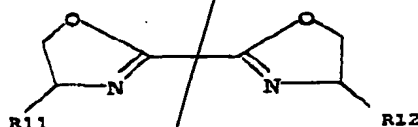
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46  
a 2-pyridine carbaldehyde imine



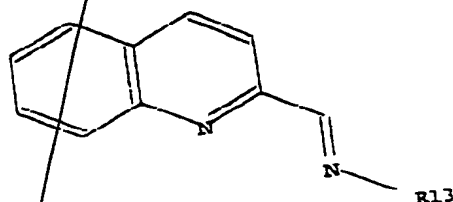
Formula 25

an oxazolidone



Formula 26

or a quinoline carbaldehyde



Formula 27

where:

$R_1$ ,  $R_2$ ,  $R_{10}$ ,  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  are independently selectable and may be selected from H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl,  $CH_2$  Ar (where Ar is aryl or substituted) or a halogen;

Handwritten notes: "A", "B", "CM", and "10".

*SN  
B  
Cr*

$R_3$  to  $R_9$  are independently selectable and may be selected from H, straight chain, branched chain or cyclic alkyl, hydroxyalkyl, carboxyalkyl, aryl,  $\text{CH}_2$  Ar, a halogen,  $\text{OCH}_{2n+1}$  (where  $n$  is an integer of 1 to 20),  $\text{NO}_2$ , CN,  $\text{O} = \text{CR}$  (where  $R$  = alkyl, aryl, substituted aryl, benzyl  $\text{PhCH}_2$  or a substituted benzyl).

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*B*

*3* A catalyst according to claim *2* wherein  $R_1$  to  $R_{13}$  are selected from *the group consisting of:*  
 $C_1$  to  $C_{20}$  alkyl,  $C_1$  to  $C_{20}$  hydroxyalkyl,  $C_1$  to  $C_{20}$  carboxyalkyl, n-propylisopropyl, n-butyl, sec-butyl, tert-butyl, cyclohexyl, 2-ethylhexyl, octyldecyl *and* lauryl.

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*a*

*9* A catalyst according to claim *3* or claim *4*, wherein the organodiimine comprises a chiral centre.

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*claim 3*

*5* A catalyst according to ~~claims 3 to 5~~ wherein one or more adjacent  $R_1$  and  $R_3$ ,  $R_3$  and  $R_4$ ,  $R_4$  and  $R_2$ ,  $R_{10}$  and  $R_9$ ,  $R_8$  and  $R_9$ ,  $R_8$  and  $R_7$ ,  $R_7$  and  $R_6$ ,  $R_6$  and  $R_5$  groups are selected from *the group consisting of* alkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl *and* cyclicaryl, containing 5 to 8 carbon atoms.

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*claim 1*

*the group consisting of*  
 6. A catalyst according to ~~any previous claim~~ wherein M is selected from  $\text{Cu(I)}$ ,  $\text{Fe(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ru(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Sm(II)}$ ,  $\text{Ag(I)}$  and  $\text{Yb(II)}$ .

*claim 1*

*the group consisting of*  
 7. A catalyst according to ~~any of claims 1 and 3 to 7~~, wherein Y is selected from  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{NO}_3$ ,  $\text{PF}_6$ ,  $\text{BF}_4$ ,  $\text{SO}_4$  and  $\text{CF}_3\text{SO}_3$ ,  $\text{CN}$ ,  $\text{SPh}$ ,  $\text{ScN}$  and  $\text{SePh}$ .

*claim 2*

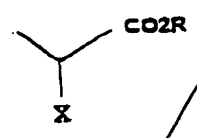
9. A catalyst according to ~~any of claims 2 to 7~~ wherein A is selected from  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{F}$ ,  $\text{I}$ ,  $\text{NO}_3$ ,  $\text{SO}_4$  and  $\text{CuX}_2$  (where X is a halogen).

*claim 1*

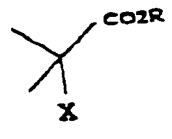
*8*  
 10. A catalyst according to ~~any previous claim~~, wherein the initiator is selected from:

RX

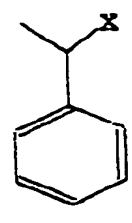
Formula 2



Formula 3



Formula 4



Formula 5

*B a*

*abs*

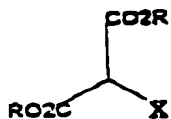
*a*

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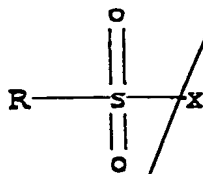
*a*  
*SH*  
*B3*

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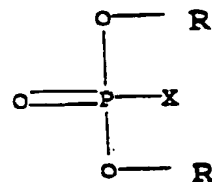
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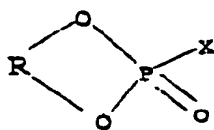
Formula 6



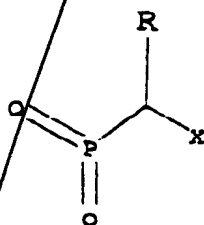
Formula 7



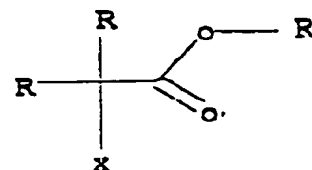
Formula 8



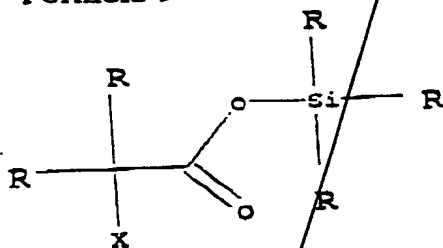
Formula 9



Formula 10



Formula 11



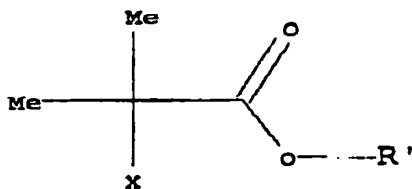
Formula 12

where R is independently selectable and is selected from straight chain alkyl, branched chain alkyl, cyclic alkyl, hydrogen, substituted alkyl, hydroxyalkyl, carboxyalkyl, aryl and substituted aryl and substituted benzyl.

X = a halide

SR  
B3  
amt

9  
11. A catalyst according to claim 10, wherein the initiator is



wherein  
where:

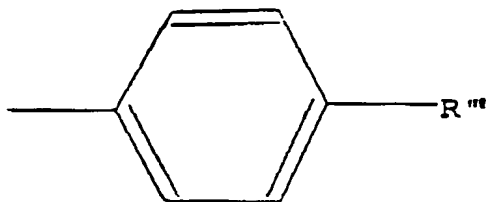
X = Br, I or Cl, preferably Br

R' = -H,

$-(CH_2)_pR''$ , where p is a whole number and R'' = H, OH,

NH<sub>2</sub>, SO<sub>3</sub>H, COOH, halide, COX, where X is Br, I or Cl,

or



R''' = -COOH, -COX, where X is Br, I or Cl, -OH, -NH<sub>2</sub> or -SO<sub>3</sub>H.

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12. A catalyst according to claim 11 wherein (b) is 2-hydroxyethyl-2'-  
bromopropionate.

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13. The use of a catalyst according to ~~any previous claim~~ in the

claim 1

sk  
B4

addition polymerisation of one or more olefinically saturated monomers.

<sup>12</sup>  
14. The use of a catalyst according to claim <sup>11</sup> 13 at a temperature between -20°C to 200°C.

<sup>13</sup>  
15. The use of a catalyst according to claim <sup>12</sup> 14 between 20°C and 130°C.

<sup>14</sup>  
16. The use of a catalyst according to <sup>claim 13</sup> ~~claims 13 to 15~~, wherein the olefinically saturated monomer is selected from methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), and other alkyl methacrylates; corresponding acrylates; also functionalised methacrylates and acrylates including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates; fluoroalkyl (meth)acrylates: methacrylic acid, acrylic acid; fumaric acid (and esters), itaconic acid (and esters), maleic anhydride; styrene,  $\alpha$ -methyl styrene; vinyl halides such as vinyl chloride and vinyl fluoride; acrylonitrile, methacrylonitrile; vinylidene halides of formula  $\text{CH}_2 = \text{C}(\text{Hal})_2$  where each halogen is independently Cl or F; optionally substituted butadienes of the formula  $\text{CH}_2 = \text{C}(\text{R}^{14}) \text{C}(\text{R}^{15}) = \text{CH}_2$  where

15

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S  
N  
B4  
cont

a



$R^{15}$  is independently H, C1 to C10 alkyl, Cl, or F; sulphonic acids or derivatives thereof of formula  $CH_2 = CHSO_2OM$  wherein M is Na, K, Li,  $N(R^{16})_4$ ,  $R^{16}$ , or  $-(CH_2)_2-D$  where each  $R^{16}$  is independently H or Cl or C10 alkyl, D is  $CO_2Z$ , OH,  $N(R^{16})_2$ , or  $SO_2OZ$  and Z is H, Li, Na, K or  $N(R^{16})_4$ ; acrylamide or derivatives thereof of formula  $CH_2 = CHCON(R^{16})_2$ , and methacrylamide or derivatives thereof of formula  $CH_2 - C(CH_3)CON(R^{16})_2$ . Mixtures of such monomers may be used.

17. The use of a catalyst, as defined in claims 1 and 3 to 12, according to claims 13 to 16, wherein the ratio (c):(a) is 0.01 to 1000 and the ratio of (a):(b) is 0.0001 to 1000.

18. The use of a catalyst as defined in claims 2 to 12 according to claims 13 to 16 wherein the ratio of Initiator is between 3:1 and 1:100.

19. The use of catalyst according to ~~claims 13 to 16~~ <sup>claim 13</sup>, where the polymerisation is undertaken in water, a protic or non-protic solvent.

20. The use of a catalyst according to ~~claims 1 to 12~~ <sup>claim 1</sup> to produce a statistical copolymer, a block copolymer, a telechelic polymer or a comb and graft copolymer of monomers according to previous claim.

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